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13. ABSTRACT (Maximum 200 words)

This program was directed toward synthesis of two closely related classes of new lithium ion conducting polymer electrolytes which are demonstrating both higher ionic conductivity and improved elastomeric properties over current state-of-the-art polymer electrolytes. The strategy exploited the approach that carbonate oxygens, within the single phase carbonate-siloxane polymer matrix, will facilitate extensive ionic dissociation of introduced lithium salts, and that furthermore elastomeric behavior of the matrix under ambient temperature conditions will lead to enhanced mobility of lithium ions. The validity of this approach was verified during this program where preliminary data supports lithium ion conductivities $> 10^{-3}$ Scm^{-1} at ambient temperature. Furthermore the elastomeric properties of these lithium ion conducting polymers will facilitate small inter-electrode distances to be achieved within portable secondary lithium batteries incorporating these new polymer electrolytes. These polymers were incorporated into lithium cells during this program.

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ADVANCED HIGH ENERGY LITHIUM POLYMER ELECTROLYTE BATTERY

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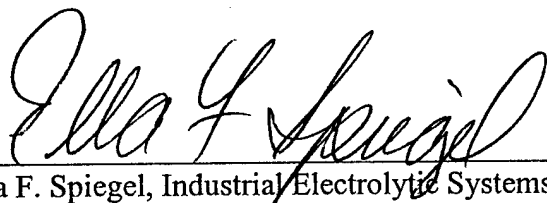
The Contractor, Eltron Research, Inc., hereby declares that, to the best of its knowledge and belief, the technical data delivered herewith under Contract No. DAAB07-98-C-G005 is complete, accurate, and complies with all requirements of the contract.

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Date

I. INTRODUCTION

The overall objective of Phase I was to synthesize two closely related classes of new lithium ion conducting polymer electrolytes which hold promise of achieving both higher ionic conductivity and improved elastomeric properties over current state-of-the-art polymer electrolytes. These materials will find application in high energy density secondary lithium batteries for portable military applications. Lithium polymer electrolytes evaluated during Phase I were based upon, i) the modification of polycarbonate molecular hosts by poly(dimethyl siloxane) and multi-functional silanes, and ii) introducing cyclic carbonates into a poly(dimethyl siloxane) matrix.

Both of these related strategies exploit the idea that carbonate oxygen, within the single phase carbonate-siloxane polymer matrix, facilitate extensive ionic dissociation of introduced lithium salts, leading to enhanced mobility by lithium ions and that furthermore a polymer matrix incorporating poly(dimethyl siloxane) would insure elastomeric behavior of the matrix under ambient temperature conditions. This would permit small interelectrode distances to be achieved within lithium batteries incorporating these new polymer electrolytes. The use of single phase polymer electrolytes can circumvent inherent mechanical restrictions of polymers currently under development based upon the respective host polymer matrices poly(acrylonitrile) (PAN), poly(vinyl chloride) (PVC) and radiation polymerized polyethers incorporating the liquids ethylene carbonate/propylene carbonate (EC/PC) as plasticizers, in which the lithium supporting electrolyte was dissolved.[1-6] For these latter polymeric electrolytes mechanical limitations within the interelectrode spacing of lithium cells can be a consequence of the two phase nature of the latter materials.[5,6] These materials are also always intrinsically 'wet' in physical appearance.

The above restrictions do not apply to carbonate-siloxane polymer electrolytes being developed in this program. The strategy used during synthesis of polymeric carbonate-siloxane matrices is summarized in Figure 1. Supporting electrolyte which was introduced into the polymer matrices was lithium trifluoromethanesulfonate.

Following verification of high lithium ion conductivity in the polymeric materials and their possessing an acceptably low glass transition temperature (T_g) consistent with maintenance of an amorphous polymer under ambient or close to ambient temperature conditions, they were

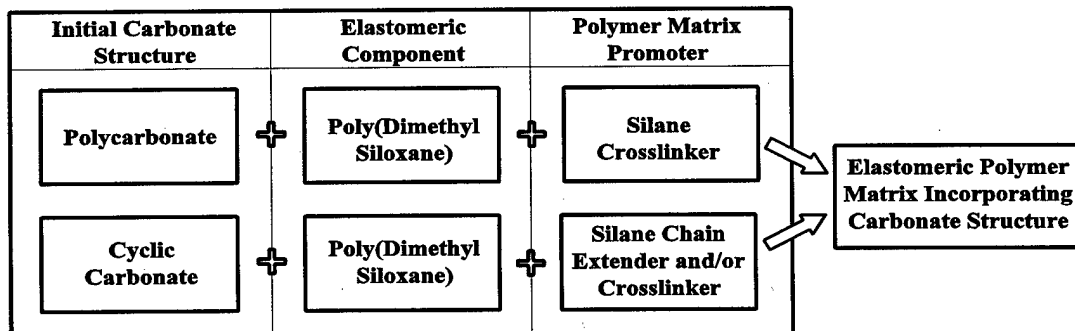| Initial Carbonate Structure		Elastomeric Component		Polymer Matrix Promoter	
Polycarbonate	+	Poly(Dimethyl Siloxane)	+	Silane Crosslinker	
Cyclic Carbonate	+	Poly(Dimethyl Siloxane)	+	Silane Chain Extender and/or Crosslinker	Elastomeric Polymer Matrix Incorporating Carbonate Structure

Figure 1. Schematic of two complementary synthetic steps performed during Phase I for preparation of carbonate-siloxane polymer matrix for lithium ion conducting polymer electrolytes.

incorporated into lithium cells possessing the general configuration $Li/Li^+polymer/V_6O_{13}$ or $LiMn_2O_4$ and their preliminary electrochemical performance evaluated. Particular emphasis is being placed in this program upon lithium ion conducting polymer electrolytes compatible for, (i) minimizing internal resistance losses within lithium cells as a result of their high ionic conductivity and ability to reliably maintain small interelectrode spacings as a result of favorable elastomeric properties, (ii) maintaining acceptable electrochemical reversibility at the lithium/polymer and polymer/V_6O_{13} interfacial regions and (iii) achieving chemical stability at respective electrode/polymer electrolyte interfacial regions.

Incentives for identification of elastomeric, lithium ion conducting polymer electrolytes possessing high ionic conductivities comes from an increasing demand for high energy density secondary batteries to be used in portable military applications. This provides a driving force for reliable, long-life, low cost, and environmentally-friendly batteries possessing both high energy and power densities. Batteries utilizing a lithium anode, a lithium ion conducting polymer electrolyte and a lithium intercalating cathode have in principle the prerequisite for meeting target battery requirements. Desired battery performance requirements correspond to respective energy and power densities of 110 Wh/kg and 40 W/kg (0.04 W/g) at an operating current density of 20 mA/cm^2.

The critical component controlling performance of such lithium batteries, which was the emphasis of Phase I, was the ability to rationally select new lithium ion conducting polymer electrolytes possessing both high ionic conductivity and acceptable elastomeric properties in single phase polymeric materials. Target ionic conductivities, under ambient conditions, were in the 10^{-3} to 10^{-2} S/cm range with ionic transport proceeding exclusively via lithium ions. Conductivities of 8×10^{-3} S/cm at ambient temperature have been preliminarily observed thus far for cyclic carbonate polymer membranes prepared at Eltron during performance of this program, a significant improvement over PEO, especially when one considers the improved elastometric properties. In particular, the use of ionically conducting polymeric electrolytes will facilitate the fabrication of thin-layer, flexible battery designs provided that the polymer can maintain a reliable interelectrode spacing absent of electronic shorting. This would contribute towards achieving low internal resistance and thereby improving electrochemical performance in terms of delivered energy density and discharge performance.

Recently, relatively high ionic conductivities have been reported[1-6] using polymeric based lithium ion conducting electrolytes where EC and PC organic solvents, incorporating dissolved lithium salts, were introduced as plasticizers and fillers into polymeric matrix of respectively PVC or PAN and radiation polymerized polyethers (so called gel or "wet" electrolytes). In spite of rather attractive lithium ion conductivities being reported at room temperature from these polymer matrices, several other technical issues have been raised. In particular the rather high weight fraction of EC and PC (up to 80%) necessary for realizing these high ionic conductivities lowers the overall realizable mechanical stability associated with reliably maintaining a small interelectrode spacing within lithium cells.

The incorporation of EC and PC as plasticizers possessing a dissolved supporting lithium salt within PAN or PVC polymer matrix is an effective strategy for introducing lithium ionic conductivity into the matrix. Current evidence suggests that ionic mediation to and from the electrode/electrolyte interfacial region is achieved exclusively via the liquid phase within the polymer matrix. Furthermore since these latter polymer electrolytes consists of a mixture of two

single phase components which are essentially inelastomeric, opportunities for conveniently achieving small interelectrode spacings in electrochemical cells are restricted.

Ideally polymer electrolytes for application in secondary lithium batteries should be single phase, providing both adequate lithium ion conductivity and polymeric homogeneity for reliably maintaining small spacings between electrodes. As a consequence Phase I was directed towards achieving high lithium ion conductivity in single phase carbonate-siloxane polymer electrolytes which also possess favorable elastomeric properties. The binding of carbonate entities to a silane based matrix were investigated as both block copolymer and as grafted side-chains. This exploited the utility of carbonate oxygen within the polymeric host facilitating effective ionic dissociation of introduced lithium salts. The presence of poly(dimethyl siloxane) insured elastomeric behavior from this single phase material. This gave improved electrochemical performance and stability for lithium batteries which incorporated these polymeric electrolytes.

Polymer electrolytes consist of polymer matrices complexed with alkali metal salts. The ability of polymers, most notably polyethers, to chelate alkali metal cations is a prerequisite for achieving ionic conduction within these materials. Inherent features that should be present in technically useful polymer electrolytes would include, i) high ionic conductivity at or close to ambient temperatures, ii) ionic transport numbers of unity for the cation of interest, iii) the ability to maintain mechanical integrity and dimensional stability within a cell subjected to electrochemical cycling, iv) possessing environmental stability, v) possessing the ability to maintain stable interfacial regions between electrodes and vi) be safe.

Incorporation of polymer electrolytes into electrochemical cells during the 1980's was restricted by inadequate ionic conductivity, with most materials possessing values between 10^{-9} to 10^{-5} S/cm at room temperature. The most widely studied material was poly(ethylene oxide) (PEO), incorporating lithium salts such as $LiClO_4$ and $LiCF_3SO_3$. This material however demonstrated ionic conductivities well below the target 10^{-3} S/cm at room temperature. Numerous other related strategies were also addressed using blends and copolymers (both, block and grafted) of various linear and cross-linked polymers,[7] including investigations by the Program Senior Physicist on poly(vinyl acetate),[8] poly(dimethyl siloxane) (PDMS) based matrices,[9-12] poly(propylene oxide)[13-16] and poly[bis(methoxyethoxy) ethoxy phosphazene], (MEEP).[17-18] Although some incremental ionic conductivity performance improvements were realized the target goal was not reached.

Insight to this time indicates segmental motion as the dominant factor influencing ionic conduction in PEO. Here ionic conduction proceeds in the amorphous phase[19] with cation transport being controlled by host polymer dynamic relaxation modes. The most probable ionic conduction mechanism involves short-range segmental motion of polymer chains together with occasional transfer of coordinated cations from one polymer strand to another.[20] Continuous, correlated motions of host polymer matrix have been simulated[21] to explain experimental convex curvature discrepancy for Arrhenius ionic conductivity temperature dependence. It has been found that anions coordinated to polyether OH$^-$ end groups are more stable than cations and form crosslinks between oxygen of adjacent chains.[22] While cation transport in amorphous polymer electrolytes occurs through strong coupling with large scale segmental motions within the host polymer, many of these materials can also exhibit substantial anionic conductivity. At present the specific nature of cation-anion interactions in polymer electrolytes, and the resultant role of the anions on mobile cation concentration and mobility, is unclear. Anion and cation transport

mechanisms within polymer electrolytes have been found dependent upon supporting electrolyte salt concentration. Cation hopping between ionic clusters and the diffusion of neutral ion pairs has been advanced as a conduction mechanism.[23]

Mixtures of EC and PC incorporated into PVC or PAN polymer matrix are generally transparent and soft whereas those with only EC or PC within polymer host possess a milky appearance and are brittle. Polymeric matrices incorporating mixtures of PC and EC are also more thermally stable than those containing pure PC, with 50:50 compositions exhibiting highest thermal stability. Although polymer electrolytes with pure PC exhibit the highest ionic conductivity, EC incorporation is essential to improve dimensional stability. Polymers containing mixed plasticizer of composition 50:50 and higher PC content can maintain a completely amorphous structure over a wide range of temperatures (-40°C to 60°C). Furthermore, mixed plasticizer compositions seem electrochemically stable.[6]

It has recently been shown that dimethyl carbonate is more stable at high anodic potentials[24] than either EC or PC based electrolytes and can be improved even further if 10 to 20% of lithium atoms are replaced by sodium.[25] While PC promotes supporting electrolyte dissociation, it is at the same time a relatively poor cation chelating agent, and a heavily swollen polymer matrix of a gel polymer electrolyte is open to deterioration by lithium ions. This can be prevented by introducing tetraethylene glycol dimethyl ether (TEGDME) since most cations (up to 90 mol%) remain bound to TEGDME.[26] However adding large fractions of organic liquid electrolytes to this polymer for improving electrochemical reversibility at polymer electrolyte/lithium electrode interface would be expected to severely compromise[27] the material advantages of polymer electrolytes. Such restrictions will be avoided in this proposed program by developing polymer electrolytes possessing both high lithium ion conductivity and good elastomeric properties for incorporation into lithium cells.

Optimization of polymer matrix towards achieving high ionic conduction is a compromise between intrinsic dielectric constant and T_g, both of which increase with increasing concentration of polar groups, but have an opposing influence upon ionic conductivity. Dielectric constant is a measure of the polymer solvating power towards introduced supporting electrolyte lithium salts.[28,29] An increase of T_g raises amorphous state temperatures to where ionic transport governed by segmental motion occurs. Higher dielectric constant also reduces ion-ion pairing, effecting both the cation concentration and the cation transport mechanism.

The solvating capacity of the polymer matrix crucially depends upon the presence of oxygen within highly flexible molecular groups along the polymer chain. The mobility of cations within such polymer matrix will be dependent upon the ability of these oxygen to coordinate with the lithium ion. This has been repeatedly demonstrated in the case of PEO.[28] Recent research on EC/PC based gel polymer electrolytes[1-6] are in support of polymer electrolytes incorporating carbonate-like structures. As we have discussed earlier the high dielectric constants of liquid EC and PC permit extensive dissociation of lithium salts and their low viscosity provides an ionic environment that facilitates high ionic mobility.[30,31]

Unmodified polycarbonates however are poor candidates for complexing with supporting electrolytes. Most of them have T_g values well above ambient temperatures and crystallize easily.[32] However the solvating power of carbonate oxygen could be preserved in a polymer matrix if segmental motion were introduced cooperatively along several monomer units. Two options for achieving this within the proposed program are, (i) modification of the polycarbonate

structure to obtain elastomeric properties, and (ii) introduction of carbonate-like structures into a known elastomer. To achieve these goals poly(dimethyl siloxane) was used as an elastomeric candidate: it is a well characterized material, it exists in an extremely broad spectrum of molecular weights and modifications, and because of numerous applications has a well developed support of polymeric reagents, catalysts, cross-linkers and chain extenders. Polysiloxanes are by far the most important inorganic backbone polymers. Their unique properties include low glass transition temperatures (several are from -120°C to -60°C), good thermal and oxidative stability, low surface energies, excellent biocompatibility and high gas permeabilities. However, the non-polar nature of typical polysiloxanes precludes their ability to ionically dissociate supporting electrolytes. As a consequence their matrix must be initially modified to become useful polymer electrolytes.[8-12,33-36] **Synthesis of carbonate-siloxane based polymer electrolytes during this program is proving an ideal strategy for achieving high lithium ion conduction within an elastomeric polymer matrix under ambient temperature conditions where preliminary lithium ion conductivities up to 8×10^{-3} Scm have been found to this time.**

II. PHASE I TECHNICAL OBJECTIVES

Specific Technical Objectives addressed during performance of this Phase I program were as follows:

- Polycarbonates with glass transition temperatures below 300 K were selected as host polymer matrices for lithium supporting electrolyte salts. This was performed by initially dissolving the polycarbonate (n_1) and lithium salt (n_2) in an organic solvent selected from THF, acetonitrile or dioxane as appropriate, where the n_1/n_2 molar ratio was systematically adjusted so that the carbonate group to lithium cation ratio could be varied between 5 and 12.

- Both promising low molecular weight polycarbonates identified above and commercial siloxane-carbonate copolymers were crosslinked with low molecular weight poly(dimethyl siloxane) and subsequently complexed with a lithium supporting electrolyte salt. This was performed by dissolving polymers of polycarbonate(n_1)/poly(dimethyl siloxane)(n_1)/silane crosslinker ($n_1/2$) and lithium salt(n_2) in selected organic solvents where n_1/n_2 ratios were systematically varied, so that the carbonate to lithium molar ratio could be adjusted between 5 and 12.

- Above polymer electrolyte compositions were subsequently cast onto a Teflon plate and cured. Their T_g and ionic conductivities as a function of temperature were determined using a conductivity cell equipped with gold electrodes specifically designed for this purpose.

- For more promising lithium ion conducting carbonate-siloxane polymer electrolytes we performed an extensive characterization. This included the temperature dependency of ionic conductivity to determine activation energy for lithium ion conduction within the polymer.

- Selected carbonate-siloxane polymer electrolytes possessing encouraging lithium ion conductivities under ambient temperature conditions were incorporated into lithium cells

possessing the general configuration $Li/Li^+polymer/V_6O_{13}$ or $Li_xMn_2O_4$.

- Perform impedance measurements are being on electrode/Li^+polymer interface to gain information on the nature of Li/Li^+ mobilities across electrode/polymer electrolyte interface.

The above Technical Objectives were experimentally addressed during Phase I by performing work in the following two tasks:

Task 1   *Synthesis of Carbonate-Siloxane Lithium Ion Conducting Polymer Electrolytes*

Task 2   *Characterization of Polymer Electrolytes and their Incorporation into Secondary Lithium Cells*

III. Phase I Research Conducted and Results Obtained

Task 1   Synthesis of Carbonate-Siloxane Lithium Ion Conducting Polymer Electrolytes

The objective of this task was i) to prepare, carbonate-siloxane block copolymer lithium polymer electrolytes by modification of polycarbonate molecular hosts by poly(dimethyl siloxane) and multi- functional silanes and ii) by introducing cyclic carbonates into a poly(dimethyl siloxane) matrix. Several polymers were synthesized using polyethylene oxide as the base polymer in order to have a control polymer electrolyte for comparison to the carbonate-siloxane block polymers which were later synthesized.

Chemicals for syntheses were as follows: polyethylene oxide (m.wt. 5,000,000), polyethylene glycol (m.wt. 8000), lithium trifluoromethane sulfonate, acetonitrile, tetrahydrofuran, petroleum ether, 2,3-dibromopropanol, Aliquat 336, potassium carbonate, potassium hydrogen carbonate, diethyl carbonate and 1,3-dibromo-2-propanol were all purchased from Aldrich. Tetraethoxy silane, methyltriacetoxy silane, methyltrimethoxy silane, platinum divinyltetramethyldisiloxane complex and poly(methylhydrosiloxane) were purchased from United Chemical Technologies. All chemicals were used without further purification. A sample of dimethyl siloxane bisphenol A carbonate block polymer was generously donated by Dr. Roger Kambour of General Electric Research and Development Center.

a. Preparation of Polyethylene Oxide Based Polymer Electrolytes

Each synthesis was set-up in an argon atmosphere dry box using a 250mL 3-neck round bottom flask. Polymer, lithium salt and crosslinking agent (Figure 2) were weighed and transferred to the round bottom flask followed by solvent addition. Oxygen/lithium ratio for each polymer did not exceed 16. Polyethylene glycol ratio to PEO was in a range of 0 - 20% for each polymer synthesized. Upon completion of reactants transfer, the flask was capped to avoid introduction of oxygen and removed from the dry box. Upon removal from the dry box the flask was flushed with argon while being equipped with an overhead stirrer in the central neck and a water jacket cooled condenser in the flask side neck. Solution was stirred for 24 hours to ensure that dissolution and crosslinking had occurred. Temperature was varied between 35-50°C depending upon solution composition. The solution was then heated to 50°C and solvent removed

under reduced pressure until a viscous polymer was present. This viscous solution was then transferred from the flask to a Teflon sheet and placed in a preheated (55°C) vacuum oven flushed with argon. Temperature was held constant and a partial vacuum of 5" applied while raising the temperature to 85°C. After 1 hour a full vacuum was applied while heating for 12 hours followed by cooling to ambient temperature and bringing it up to atmospheric pressure while flushing with argon. When atmospheric pressure and ambient temperature were reached the polymer was immediately transferred to the dry box for storage in an inert atmosphere. Compositions, solvents and reaction temperature for each PEO polymer are summarized in Table 1.

b. Dimethyl Siloxane Bisphenol A Carbonate Block Polymer

Experiments were performed using a 250mL 3-neck round bottom flask. Dimethyl siloxane bisphenol A carbonate block polymer (Figure 3), crosslinker (Figure 2, if used) and lithium trifluoromethane sulfonate were weighed and transferred to this round bottom flask followed by addition of 41mL tetrahyrofuran. Composition of each polymer is summarized in Table 2. Oxygen/lithium ratio for this polymer mixture was 8. Molecular weight of dimethyl siloxane bisphenol A carbonate block polymer was 4000. Upon completing reactant transfer the flask was capped to avoid introduction of oxygen and flushed with argon. The flask was placed in an oil bath for heating and equipped with an overhead stirrer in the central neck and a water jacket cooled condenser in the side neck of the flask. Solution was stirred for 24 hours to ensure that dissolution had occurred. The temperature was held at 35°C during the first 12 hours. Solution was then heated to 40°C and solvent removed under reduced pressure until a slightly viscous polymer solution was present. Viscous solution was then transferred from the flask to a Teflon sheet and placed in a preheated (40°C) vacuum oven flushed with argon. Temperature was
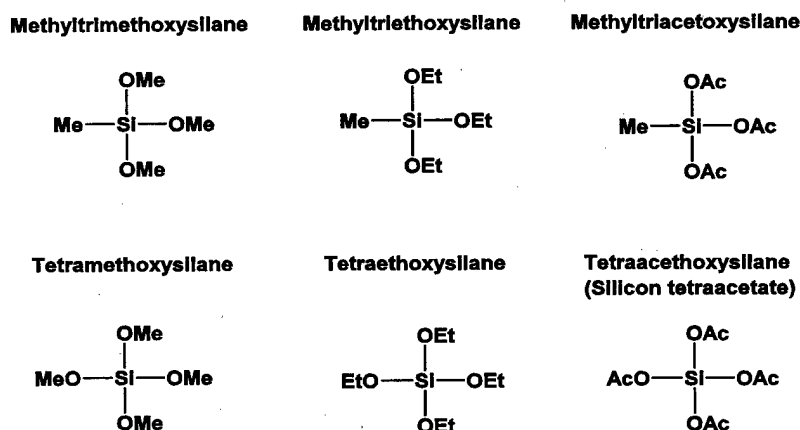

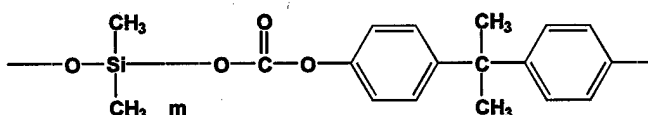**Figure 2.** Crosslinkers evaluated during Phase I.

Figure 3. Dimethyl siloxane, bisphenol A carbonate block copolymer.

Table 1.
Polyethylene Oxide Polymer Compositions Evaluated During Phase I

Polymer #	Polymer (g)	Crosslinker Methyltriacetoxy silane (g)	LiCF₃SO₃	Solvent CH₃CN (mL)	Temp. (°C)
PO201	PEO - 1.32	None	0.29	83	35
PO301	PEO - 1.32	None	0.29	83	35
PO401	PEO - 1.30	0.03	0.29	70	45
PO601	PEO - 1.06 PEG - 0.27	None	0.29	70	35
PO701	PEO - 0.93 PEG - 0.26	0.13	0.27	70	50
PO702	PEO - 0.93 PEG - 0.26	0.13	0.27	70	45
PO801	PEO - 1.34	none	0.60	84	45
P0901	PEO - 0.940 PEG - 0.270	0.14	0.55	70	44

Table 2.
Composition of Bisphenol A Carbonate Block Polymer Electrolytes
Prepared During Phase I

Polymer #	Bisphenol A Carbonate Block Polymer	Crosslinker Methyltriacetoxy silane	Lithium Salt LiCF₃SO₃	Solvent (mL) THF	Temp. °C
P1003	0.5600	-0-	0.2845	41	35
P1101	0.5608	0.0622	0.0540	34	35
P1201	0.6682	0.0700	0.1199	41	35
P1501	bisphenol A 0.56 ❖PDSS: 0.12	0.0622	0.0523	45	35

❖PDSS Polydimethylsiloxane, silanol terminated

held constant and the oven was purged with argon under a slight pressure. After 12 hour a slight vacuum was applied while heating, then a full vacuum was applied for 2 hours. The oven was cooled to ambient temperature and brought up to atmospheric pressure while flushing with argon. When atmospheric pressure and ambient temperature were reached the polymer was immediately transferred to the dry box for storage in an inert atmosphere.

c. Cyclic [(allyloxy)methyl]ethylene Ester Carbonic Acid

The procedure for preparation of cyclic[(allyloxy)methyl]ethylene ester carbonic acid[37] (CAMEECA) is shown in Figure 4 which involved formation of the cyclic carbonate in the allyloxy chain to give CAMEECA. A 1000ml round bottom flask was used as the reaction flask. To this flask was added 3.17 mol (384mL) diethyl carbonate, 1.554 mol (192mL) of 3-(allyloxy)-1,2-propanediol, and 32g of K_2CO_3 (dried in the oven prior to use). The flask was equipped with a magnetic stir bar and a Dean Stark trap which was fitted with a water cooled condenser and used to collect ethanol as it formed *in-situ* during the reaction sequence. The reaction mixture was heated to 120°C for 24 hours and during this time 200mL of ethanol was collected. Upon completion the mixture was cooled to room temperature and filtered to remove carbonate solids present in solution. A Welch-DuoSeal (Model 1402.F) was used for vacuum distillation. Prior to use the vacuum pump was tested to determine its efficiency and using the fractional distillation setup we were able to reach 12 Torr. Due to the viscosity and high boiling point of the product ~250°C it was necessary to reach a relatively low vacuum. Three fractions were removed during the fractional distillation corresponding to:

Fraction 1.   Temperature - 30°C excess diethyl carbonate
Fraction 2.   Temperature - 134 - 144°C excess starting material
Fraction 3.   Temperature - 150 - 152°C product

Proton (H) NMR's were performed on fractions 2 and 3 using 0.1mg sample in 0.6mL $CDCl_3$. Fraction 2 was unreacted starting material and fraction 3 proved to be the desired product. Signals were compared with those found in the literature and were as follows: ^1H NMR ($CDCl_3$): δ5.86 (m, 1H, C=CH), δ 5.25 (m, 2H, CH_2=C), δ 4.81 (m, 1H, CCH(C)O), δ 4.48 (m, 2H, CCH_2O), δ 4.05 (d, 2H, OCH_2C=C), δ 3.66 (m, 2H, CCH_2O). NMR analysis concluded that the desired product was obtained in 56.7% yield. This material was used as a precursor for the synthesis of poly{[3-[2,3-(carbonyldioxy)propoxy]propyl]methyl siloxane} as described in the following subsection.
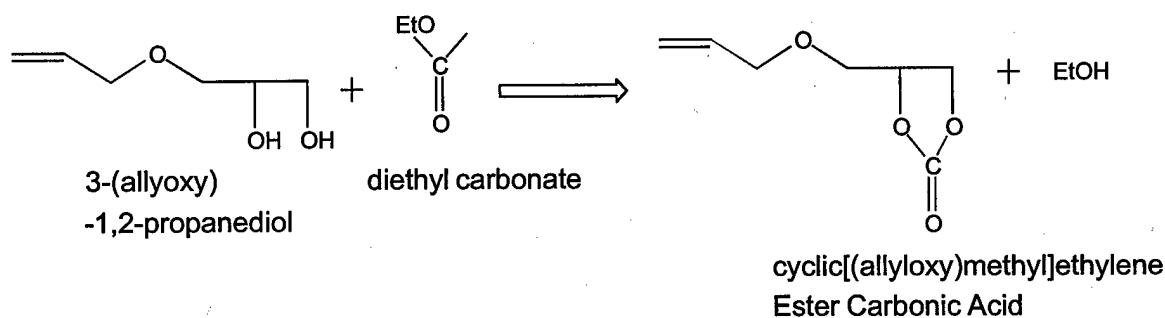

Figure 4.   Synthetic scheme used to synthesize CAMEECA.

d. Synthesis of Poly{[3-[2,3-(carbonyldioxy)propoxy]propyl]methyl siloxane}

The overall reaction scheme followed for synthesis of poly{[3-[2,3-(carbonyldioxy)propoxy]methyl siloxane}is shown in Figure 5. Synthesis preceded using a two neck 150 mL round bottom flask equipped with a magnetic stir bar, condenser and thermometer

to which was added 2.0039g (0.033mmol) of poly(methylhydrosiloxane)[PMHS], 5.2677g (0.033 mmol) of cyclic[(allyloxy)methyl]ethylene ester carbonic acid and 20 mL of acetonitrile. Several different molecular weights of polymethylhydrosiloxane (Figure 6) were evaluated during this synthesis to determine what influence they would have on membrane stability and elasticity. Grade PC 119 (mol. wt. 1500) and PS 120 (mol. wt. 2270), which are terminated with methyl groups have been evaluated thus far. The flask was heated to 60°C using a heating mantle. To the stirred solution was added 4 drops of platinum divinyltetramethyldisiloxane (2-3% platinum concentration in xylene) catalyst. Upon addition of platinum catalyst the solution turned cloudy and then became clear within a few minutes. The reaction was stirred and heated for 16 hour followed by cooling to room temperature.
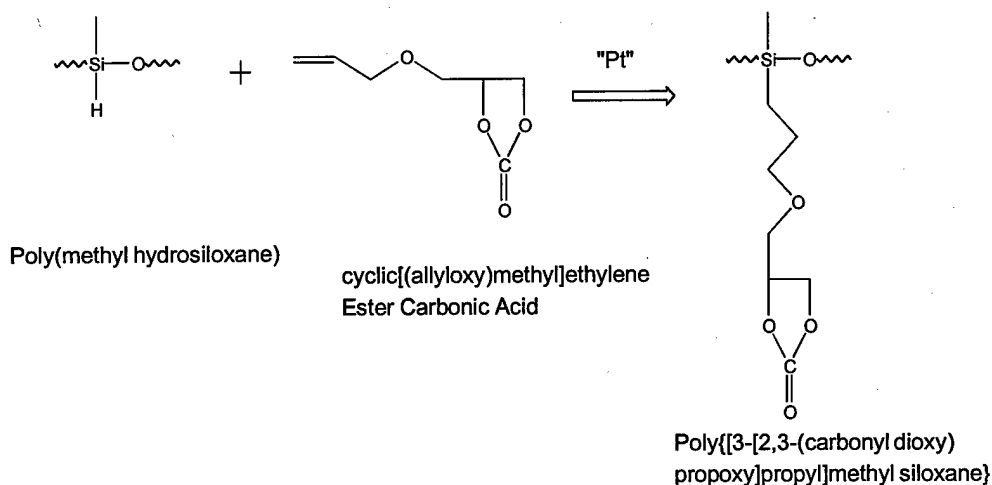

Poly(methyl hydrosiloxane)

cyclic[(allyloxy)methyl]ethylene
Ester Carbonic Acid

Poly{[3-[2,3-(carbonyl dioxy)
propoxy]propyl]methyl siloxane}

Figure 5.   **Scheme for synthesis of Poly{[3-[2,3-(carbonyl dioxy)propoxy] propyl] methyl siloxane.**

An FTIR spectrum was taken which indicated that the SiH IR band at $2160cm^{-1}$ had diminished. Solvent was removed by rotary evaporation, then the polymer was purified by precipitation into a 90/10 (v/v) mixture of hexane and acetone. Product appeared as a viscous grainy solid which was then pumped on under reduced pressure for 24 hours to remove any residual solvent. A sample was prepared for proton NMR analysis using acetone-d_6. Results were as follows: δ 4.96 (1H, CCH(C)O), 4.37 (2H, CCH$_2$O), 3.74 (2H,OCH$_2$CO), 3.51 (2H,OCH$_2$), 1.70 (2H, CH$_2$), 0.62 (2H, CH$_2$Si) and 0.19 (3H, SiCH$_3$). NMR results conclude that this polymer was the desired product poly{[3-[2,3-(carbonyldioxy)propoxy]propyl]methyl siloxane}. Resulting cyclic polycarbonates were then condensed with silane crosslinkers (Figure 2).
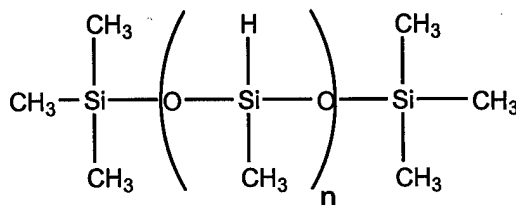

Figure 6.   **Polyhydromethylsiloxane (methyl terminated). Evaluated during Phase I in the synthesis of carbonate-siloxane copolymers.**

e. Synthesis of Crosslinked Cyclic Carbonate Siloxanes

Poly{[3-[2,3-(carbonyldioxy)propoxy]propyl]methyl siloxane} made from the synthesis described in Section d was used as the precursor in conjunction with various silane crosslinkers or chain extenders and lithium salts to form new polycarbonate polymer electrolytes for evaluation in secondary lithium rechargeable batteries. Synthesis of various polycarbonates was carried out by transferring starting materials for example: 0.4900g - Poly{[3-[2,3-(carbonyldioxy)propoxy]propyl]methyl siloxane}, 2.410g - methyltriacetoxysilane, 0.1090g $LiCF_3SO_3$ and 46mL acetonitrile, to a 250 mL round bottom flask equipped with a condenser and overhead stirrer. When reactants were dissolved in solution a catalyst such as acetic acid was added to facilitate the crosslinking reaction. A typical crosslinking reaction is illustrated in Figure 7. Polymethylhydrosiloxane (Figure 6) used in Section d was terminated with methyl groups. Addition of acetic acid during synthesis of crosslinked cyclic carbonates facilitates the formation of OH groups which react with the methyltriacetoxysilane as shown in Figure 7. Solution was heated to 50°C while stirring for 12 hours then raised to 60°C. Solvent was removed by vacuum distillation until a viscous solution was obtained. This viscous solution was then poured onto a Teflon plate and placed into a vacuum oven to remove solvent under an argon atmosphere for 1 hour before applying vacuum. Full vacuum (25 in Hg) was applied and oven heated to 70°C to cure the polymer for 24 hours. Upon completion of curing the polymer was removed from the oven and characterized using in-house instrumentation to be discussed in detail in Task 2. Polymers made thus far, utilizing this precursor polymer are summarized in Table 3.

Figure 7. **Representation of crosslinking reaction with methyltriacetoxysilane.**

f. Synthesis of Hydroxy and Hydroxy Methyl Ester Carbonic Acid

Several synthetic routes were evaluated in an effort to prepare five and six membered cyclic carbonates shown in Figure 8. It was envisioned that these cyclic carbonates could be prepared by reacting K_2CO_3 with the corresponding alkyl dihalides via the overall reaction:[38]
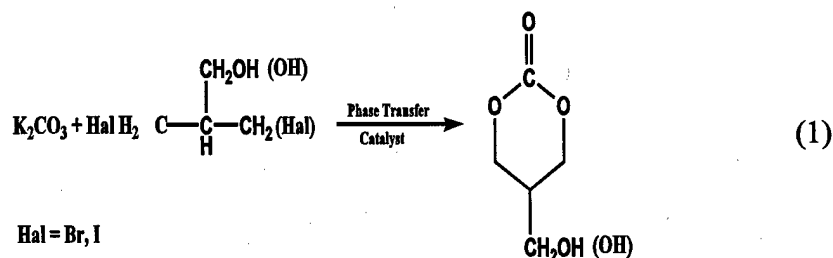

(1)

Table 3.
Composition of Cyclic Carbonate Siloxane Polymers Evaluated in This Program

Polymer #	Polymer (g)	Crosslinker(g)	Lithium salt (g) LiCF₃SO₃	Solvent (ml)	Catalyst (drops)	Temp (°C)
P1301	*PCPPMS/ 0.49	◆MTAS/0.24	0.11	ACN 46	Pt/1	45
P1302	*PCPPMS/0.49	◆MTAS/0.24	0.11	THF 46	acetic acid 1	50
P1303	*PCPPMS/0.50	◆MTAS/0.25	0.11	ACN 46	acetic acid 1	45
P1401	*PCPPMS/0.50	◆MTAS /0.24	0.15	ACN 15 Benzene 28	acetic acid 2	50
P1601	*PCPPMS/0.59 ❖PDSS/0.087	◆MTAS/0.073	0.14	ACN 15 Benzene 28	acetic acid 2	50
P1701	*PCPPMS/0.64	•VMDAS/0.040	0.12	ACN 15 Benzene 28	acetic acid 2	65
P1801	*PCPPMS/0.63	•VMDAS/0.037 ◆MTAS/0.074	0.116	ACN 34 Benzene 66	Pt/4	60
P1901	CAMEECA/5.269 PHMS/1.003	◆MTAS/3.681	0.673	ACN 40	Pt/4	65

* PCPPMS Poly{[3-[2,3(carbonyldioxy)propoxy]propyl]methylsiloxane
❖PDSS = Polydimethylsiloxane, silanol terminated, ◆MTAS = methyltriacetoxysilane
•VMDAS = vinylmethyldiacetoxysilane, ACN = acetonitrile

A two neck 250 mL round bottom flask was equipped with a magnetic stir bar, thermometer and condenser. To this flask was added 0.500 mol (51.4mL) 2,3-dibromopropanol, 4 mmol Aliquat 336, 10g $KHCO_3$, 14g K_2CO_3 and 50mL of petroleum ether. The reaction mixture was heated to 100°C while stirring for 16h. The reaction mixture was cooled to room temperature and filtered to remove all solids. Liquid filtrate was purified by vacuum distillation under reduced pressure at 12 Torr. Several fractions were collected then redistilled. Fractions were analyzed by proton NMR but the largest fraction proved to be the starting material which indicated that this product was difficult to obtain. It was thought that these reactions pathways would lead to initial synthesis of five and six membered cyclic carbonates. This synthetic procedure was not, however, found successful and as a consequence was not pursued further.

Successful completion of this task resulted in the synthesis of a polysiloxanes bearing cyclic carbonate side chains which could dissolve lithium salts and exhibit high ionic conductivity at room temperature with T_g well below ambient temperature. Polysiloxanes were selected as the main structure to which the cyclic carbonate was bonded because they are flexible polymers with low T_g. The carbonate oxygen within the single phase carbonate-siloxane polymer matrix facilitates extensive ionic dissociation of lithium salts leading to enhanced mobility by lithium ions. This has resulted in synthesis of polymers capable of dissolving lithium salts which are flexible at ambient temperature.
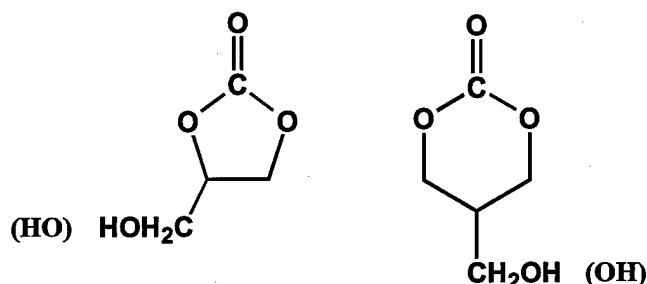

Figure 8. **Five and six cyclic carbonates used during Phase I towards preparation of poly(carbonate siloxane) polymer electrolytes.**

Task 2 Characterization of Polymer Electrolytes and Their Incorporation into Secondary Lithium Cells

Procedures followed for characterization of the subject carbonate-siloxane based polymer electrolytes will now be discussed.

a. Glass Transition Temperature of the Polymer Matrices.

The ability to maintain high lithium ion conductivity in carbonate-siloxane polymer electrolytes was dependent in-part upon identifying polymeric materials with glass transition temperatures (T_g) which occurred below ambient temperatures. Glass Transition and melting point were determined using a DuPont 9900 Differential Scanning Calorimeter. Operating conditions were as follows: sample size - 2.9mg; temperature ramp rate - 10°C/min; inert gas - argon; gas flow rate - 10 mL/min; initial temperature -150°C and final temperature 150°C. Preferred polymer electrolytes were selected with T_g values either below or close to ambient temperatures. Results for each polymer evaluated are summarized in Table 4.

Table 4.
Properties of Polymer Electrolytes Evaluated During Performance of the Phase I Program

Polymer #	Ionic Conductivity (S/cm) (25°C)	Ionic Conductivity (S/cm) (60°C)	Glass Transition Temperature °C	Melting Point °C
PO302	6.5×10^{-7}	3.9×10^{-6}	-41.35	63.16
PO401	5.1×10^{-6}	1×10^{-4}	-42.72	61.91
PO601	4×10^{-6}	NA	-31.55	62.72
PO701	3×10^{-6}	NA	-42.10	60.64
PO702	3×10^{-7}	NA	-42.81	62.26
PO802	5.3×10^{-7}	5.2×10^{-5}	-40.05	61.32
P1003	7×10^{-9}	NA	62.35	169.73
P1101	4.3×10^{-6}	4.53×10^{-6}	56.20	233.14
P1201	4.43×10^{-6}	4.59×10^{-6}	57.65	NA
P1302	7.99×10^{-3}	3.69×10^{-2}	-21.69	135
P1303	1.39×10^{-6}	6.28×10^{-6}	-26.77	NA
P1401	2.6×10^{-4}	1.8×10^{-3}	-44.2	124.1
P1501	8.11×10^{-7}	8.54×10^{-7}	-47.2	56.5
P1701	8.66×10^{-6}	7.88×10^{-5}	-23.4	NA
P1801	5.15×10^{-4}	1.24×10^{-3}	-53.9	123.6
P1901	2.21×10^{-5}	7.43×10^{-5}	-28.2	NA

b. Polymer Electrolyte Ionic Conductivities.

The overall ionic conductivity of carbonate-siloxane lithium ion conducting polymer electrolytes prepared during performance of Task 1 were interpreted by a configuration entropy model given by:

$$\sigma = AT^{-1} \exp (-B/(T-T_o)) \tag{2}$$

where A was proportional to the number of charge carriers and T_o was related to the polymer glass transition temperature (T_g).[39,40] Conductivity cells (Figure 9) were prepared by placing polymer electrolytes between two electronically conducting gold electrodes which were deposited onto glass slides. Glass microscopic slides were first deposited with chromium using an Edwards Coating
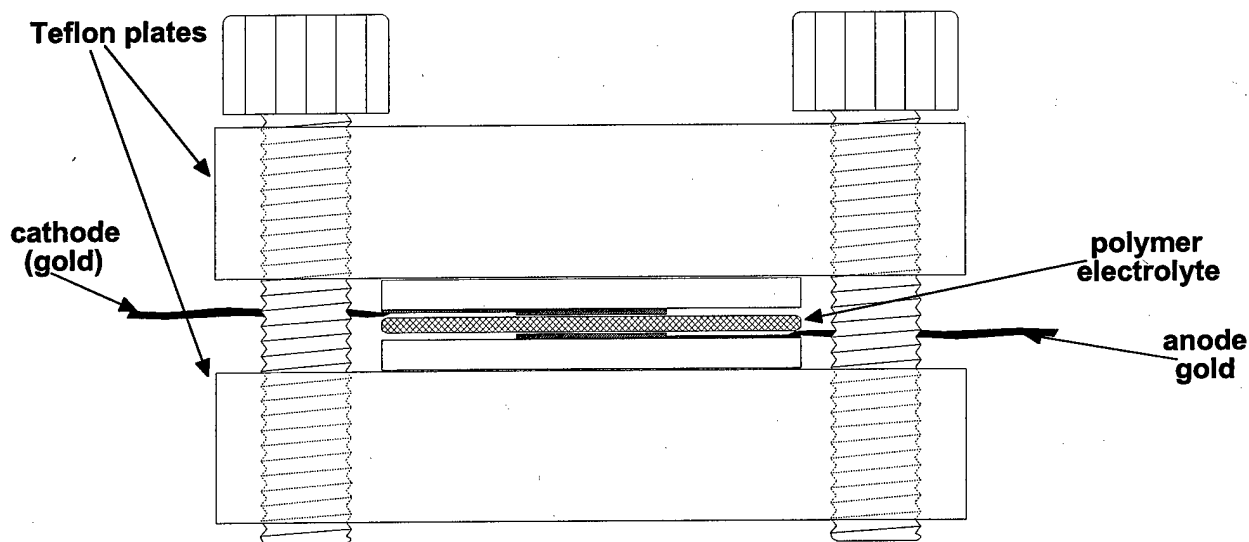
Figure 9.   **Schematic of cell used for conductivity mesurements.**

System Model E306A at 1 Å/sec until a thickness of 100Å was deposited to provide a rough surface for the gold to adhere to. Gold was deposited at 1-2 Å/sec until a total thickness of 1000Å was reached. A pattern was shaped from a mask which enabled four electrodes to be deposited simultaneously onto a microscopic glass slide. The area of each electrode was $0.196cm^2$. Electrodes were positioned between two 1" x 1" acrylic or Teflon plates which contained modine screws in each corner to facilitate introducing uniform pressure across the polymer electrolyte surface area.

Polymer electrolyte ionic conductivity measurements were based on the fact that the high frequency limit of the complex impedance was generally equal to electrolyte resistance.[41] Electrolyte conductivity, σ was then derived from series resistance, R_s, electrode surface area, A, and polymer electrolyte membrane thickness d, from $\sigma = d/(A \cdot R_s)$. Conductivity measurements were in support of exclusive ionic conductivity due to values being temperature dependent activation controlled over the temperature range 20 to 75°C. Ionic mobility above their glass transition temperatures indicated an activation energy of 0.2···0.7 eV as we had anticipated for these rubbery polymers.[42]

In these measurements the series resistance represents all ohmic contributions (i.e. current collectors, electronic resistance contributions and interfacial ohmic drop). In particular the measured interfacial resistance was noticed when cell polarization potential was varied from 0 to 3.5 V: resistance had a minimum at about 2.5 V.[42] However, this resistance contribution corresponded to $\leq 10\%$ of total measured values. Impedance measurements were conducted using an electrochemical impedance arrangement comprising a PAR Potentiostat/Galvanostat Model 273 and a Schlumberger SI 1260 Impedance/Gain-Phase Analyzer. The conductivity cell was assembled in a dry box under an argon atmosphere and placed in a self contained glass holder (Figure 10) equipped with lead wires to make contact for both the working and counter electrode outside the cell. Upon removal from the dry box the apparatus was placed in a Faraday cage to avoid spurious electrical noise. The cell was heated by placing in a jacketed beaker through which heated oil was circulated for temperature control. The experiment was computer controlled, and complex impedance parameters acquired and analyzed by Zplot software. An ac voltage amplitude
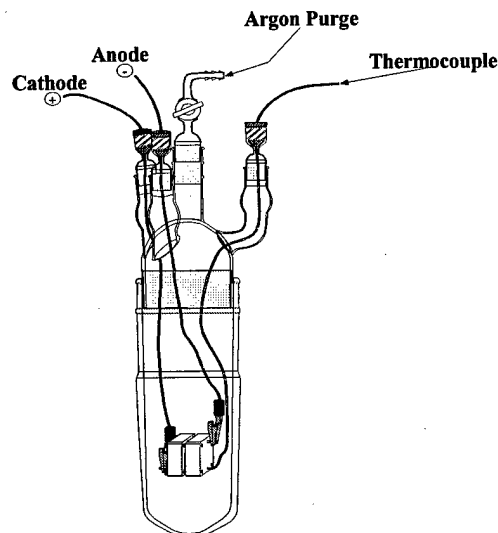
Figure 10. Schematic of glass apparatus used as an inert atmosphere
chamber for conductivity cells.

of ± 10 mV was used in a potentiostat mode to ensure only a small perturbation of polymer electrolyte steady-state conditions. Since only series resistance of the electrolyte was of interest, the frequency was limited to the 100 kHz - 1 Hz range. Resulting ionic conductivity values for polymer electrolytes are summarized in Table 4.

c.   *Incorporation of Preferred Polymer Electrolytes into Lithium Cells and Preliminary Electrochemical Testing.*

The objective here was to systematically identify preferred electrode fabrication and lithium cell assembly techniques which be eventually adapted in the preparation of solid-state lithium cells incorporating the subject carbonate-siloxane polymer electrolytes possessing practical electrochemical performance characteristics. Preparation of cathode materials used in battery assemblies will now be discussed.

i. $LiMn_2O_4$ Preparation.

Li_2CO_3 2.0320 g (0.0271 mol) and 12.649g (0.1100 mol) $MnCO_3$ were transferred to a 100mL Nalgene bottle which contained 25mL of ethanol and 4 ceramic balls. The heterogeneous mixture was ball milled for 24 hour. Ethanol was removed by evaporation and resulting powder ground and calcined by ramping 5°C/min to 800°C and holding that temperature for 24 hour followed by cooling to ambient temperature at 5°C/min. Powder was ground and analyzed by XRD which confirmed as $Li_xMn_2O_4$. Cathode constituents corresponded to 1) Polyethylene oxide(PEO)/ $LiCF_3SO_3$ (70:30 ratio w/w), 2) (PEO/$LiCF_3SO_3$)/Carbon(Vulcan VXC72RGP-3540) (50:50 ratio w/w), 3) $LiMn_2O_4$/[(PEO/$LiCF_3SO_3$)/carbon]/carbon (55:35:10 ratio w/w) and was ball-milled for 16 hours to ensure adequate mixing.

ii. V₆O₁₃ Preparation.

ii. V₆O₁₃ Preparation.

V_2O_5 3.1090g (0.292 mol) and vanadium metal powder 5.9499g (0.1168 mol) were placed in a ceramic container and calcined by ramping at 3°C/min to 700°C and holding at temperature for 12h. The calcined powder was then ground to a fine powder. Powder was analyzed by XRD to confirm that the desired metal oxide was formed.

V_6O_{13} cathodes were prepared incorporating the lithium conducting polymer electrolyte as a strategy for both increasing cathode Faradaic utilization and improving bonding to the polymer electrolyte. In this case cathode constituents corresponded to 1. Polyethylene oxide(PEO)/ $LiCF_3SO_3$ (70:30 ratio w/w), 2. (PEO/$LiCF_3SO_3$)/Carbon(Vulcan VXC72RGP-3540) (50:50 ratio w/w), 3. V_6O_{13}/[(PEO/$LiCF_3SO_3$)/carbon]/carbon (55:35:10 ratio w/w). Each mixture was ball milled for 16 hours to ensure adequate mixing before proceeding to the next step. Cathodes from this material were obtained by pressing the cathode mixture onto a expanded nickel mesh which acted as the substrate and current collector. Cathode mix was evenly spread onto the nickel mesh substrate to form a 1cm² electrode area followed by pressing between 10,000 and 15,000 psi. Polymer electrolyte curing within these electrodes was performed by heating under vacuum at temperatures between 90 and 120°C.

Onto one surface of the V_6O_{13} cathode disk was placed a preferred carbonate-siloxane polymer electrolyte as a thin-film absent of any pinhole defects. The previous incorporation of polymer electrolytes within the cathode matrix prior to cell assembly was expected to assist in providing an effective bond at the cathode/polymer electrolyte interface. Final lithium cell assembly was performed within a dry box under an Ar atmosphere. Cells were prepared by lightly pressing a lithium electrode to the polymer electrolyte/cathode assembly.

Lithium cells prepared during performance of this task possessed the respective configurations:

$$Li / P0301 / V_6O_{13}$$
$$Li / P0301 / LiMn_2O_4$$
$$Li / P1801 / V_6O_{13}$$
$$and$$
$$Li / P1801 / LiMn_2O_4$$

These cells, which were electrochemically cycled under ambient temperature conditions possessed open circuit potentials in the ≈ 3.5 V range. Since these cells were assembled towards the end of the Phase I program no time was available for long-term cycling to be performed.

IV. Conclusions and Future Work

This program is addressing the synthesis of carbonate-siloxane polymer electrolytes to achieve higher ionic conductivity and improved elastomeric properties over currently available polymer electrolytes. Work performed during this Phase I program included initial investigations utilizing PEO to develop techniques for synthesizing and curing polymers. PEO polymer films were then characterized by DSC to determine glass transition temperature (T_g) and ionic conductivity measurements. Our results were in close agreement to those listed in the literature

which indicated that synthetic technique and characterization methods were satisfactory. Research was then focused on the synthesis of cyclic carbonate siloxane precursors which were then reacted with specific crosslinking agents and lithium salts to form new carbonate-siloxane polymer electrolytes. Upon completion of synthesis each polymer electrolytes were fully characterized by NMR, FTIR, DSC and impedance spectroscopy.

Initial investigations of carbonate polymers utilized dimethyl siloxane bisphenol A carbonate block polymer (mol wt 4000) which was supplied by Dr. Roger Kambour of General Electric Research and Development Center. This polymer is a white granular powder of relatively low density which readily dissolves in acetonitrile or tetrahydrofuran. Lithium trifluoromethane sulfonate was utilized as the lithium ion conductor for the polymer matrix. After several attempts a flexible, stable polymer film was formed at ambient temperature. Characterization of the bisphenol A polymer films gave T_g between 50 - 60°C and ionic conductivities in the range of 10^{-8} to 10^{-9} Scm^{-1}. Results indicate that this material, though flexible and stable at room temperature, did not act as an effective lithium ion conductor and therefore was not suitable for this application.

The major conclusion for work completed during Phase I has shown promising results for the application of carbonate-siloxane polymer electrolytes in lithium rechargeable batteries. Carbonate siloxane polymer films that have been synthesized at Eltron are thin films (0.07 - 0.10 mm) with each having a T_g below 300 K. Polymers films which have been evaluated are soft and slightly tacky at room temperature which allows them to adhere to the electrode surface therefore eliminating the necessity to laminate the polymer to the electrode surface. Research completed to date has focused on polymerization of poly{3[2,3-(carbonyldioxy) propoxy]propyl]methyl siloxane with crosslinkers such as methyltriacetoxysilane, and lithium trifluromethanesulfonate used as the primary lithium salt. A dispersion polymerization was initiated using several different catalysts to facilitate the reaction to form polysiloxane carbonates that are flexible and possess a lithium ion conductivity up to 8×10^{-3} Scm^{-1} at ambient temperature.

Initial studies were focused on polyethylene oxide (PEO) to develop techniques for pouring polymer films as well as curing and characterization. During evaluation of ionic conductivity of PEO polymer films we observed that conductivity improved as the polymer was cycled through a temperature range of 25°C - 60°C. This indicates stability over time and the ability to facilitate lithium ion transport. Results shown in Figure 11A indicate the excellent conductivity of the cyclic carbonate polymer (p1801) as compared to the PEO (P0302 and the bisphenol A carbonate block polymer (P1801). Polymer P1801 was also crosslinked with a chain extender (vinylmethyldiacetoxysilane) and crosslinker (methyltriacetoxysilane) to determine what influence this would have on the polymer. Results in Figure 11B indicate overall improvement in the ionic conductivity. This synthetic pathway will be explored in more detail in Phase II. These studies have helped in understanding the polymer system and the influence of crosslinkers and chain extenders. Polymer P1302 (prepared from polysiloxane and cyclic carbonate crosslinked with methyltriacetoxysilane) had ionic conductivities up to 7.99×10^{-3} Scm^{-1} at 25°C showing marked improvement over PEO based polymers. The temperature dependent lithium conductivity for cyclic carbonate polysiloxane polymers showed reversibility whereas the response of PEO based polymers behaved exponentially indicating decomposition at higher temperatures. This was a very encouraging result for our polysiloxane-cyclic carbonate polymer electrolytes thereby verifying validity for the originally proposed strategy.
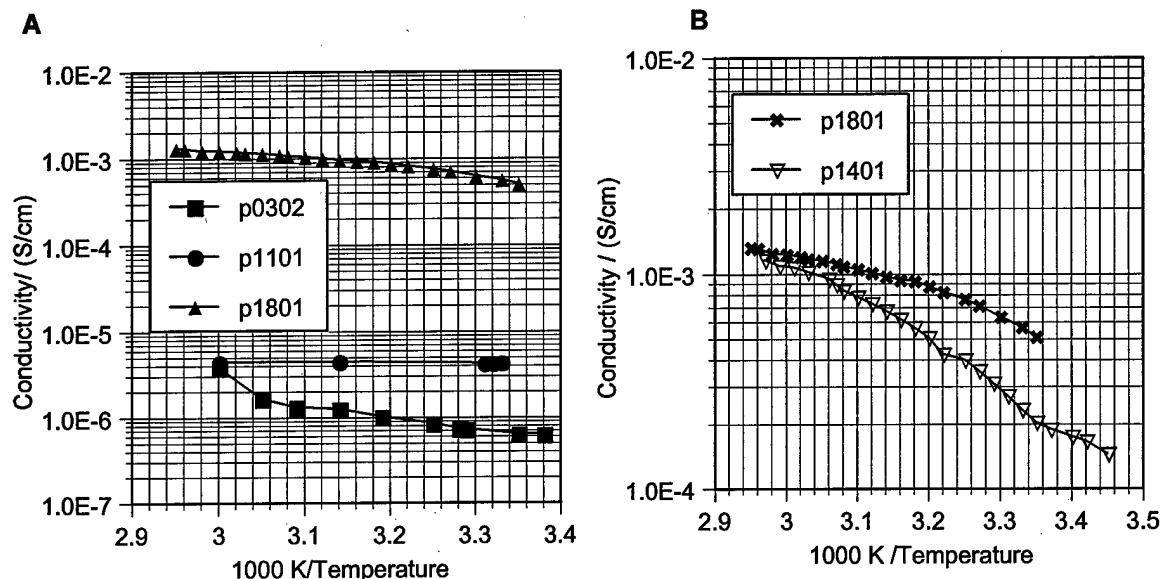
A   B

Figure 11. (A) Conductivity comparisons for PEO (po302), Bisphenol A carbonate block (p1101) and cyclic carbonate polymer (p1801). (B) Comparison of two cyclic carbonate polymers with (p1801) and without (p1401) a chain extender in the polymer matrix.

Polymers prepared from poly{3[2,3-(carbonyldioxy) propoxy]propyl]methyl siloxane a polysiloxane with cyclic carbonate side chains has shown promising results for battery applications. This polymer was crosslinked with methyltriacetoxy silane and incorporates lithium trifluoromethanesulfonate into the polymer matrix as the ion conductor. Polymers were prepared using various solvent systems and temperatures in order to produce a polymer film with the desired properties for this application. Our best polymer made from the precursor poly{3[2,3-(carbonyldioxy) propoxy]propyl]methyl siloxane, exhibits a T_g in the range of -22°C and preliminary ionic conductivities of 7.99×10^{-3} Scm^{-1} at 25°C and 3.69×10^{-2} Scm^{-1} at 60°C which indicates that this material has distinct possibilities in lithium battery applications. Texture, stability and flexibility are dependent upon the crosslinker and solvent system used for each polymer composition.

V. Summary of Phase I Results

- Polysiloxanes with cyclic carbonate side chains were prepared by hydrosilation of poly(hydromethylsiloxane) with cyclic[(allyloxy)methyl]ethylene ester carbonic acid. This precursor was then further reacted with selected crosslinkers and lithium salts to form polycarbonates with glass transition temperatures below 300K. This was performed by initially dissolving the polycarbonate (n_1) and lithium salt (n_2) in THF or acetonitrile as appropriate, where the n_1/n_2 ratio of the carbonate group to lithium cation ratio for polymers evaluated was 8.

- Dimethyl siloxane Bisphenol A carbonate block polymer was crosslinked with

methyltriacetoxy silane and complexed with lithium trifluoromethanesulfonate which acted as a supporting electrolyte salt. This was performed by dissolving bisphenol A carbonate block polymer (n_1)/silane crosslinker $(n_1/2)$ and lithium salt(n_2) in tetrahydrofuran where n_1/n_2 ratios were systematically varied carbonate to lithium molar ratio which was adjusted between 4 and 8.

- Attempts were made to prepare five and six membered cyclic carbonates possessing CH_2OH and OH^- groups from K_2CO_3 and alkyl dihalides. We have discovered that short chain dialkyl halides will not readily form cyclic carbonates.

- Preferred polymer electrolyte compositions were subsequently cast onto a Teflon plate and cured. Techniques were developed for each polymer that was prepared to define a viscosity and pouring temperature that would yield a thin (0.07-0.10mm), flexible polymer film. Temperatures, curing time and vacuum were dependent upon polymers and solvents used during each preparation.

- Glass transition (T_g) and melting point were determined using a DuPont 9900 Differential Scanning Calorimeter. Operating conditions were as follows: sample size - 2.9mg; temperature ramp rate - 10°C/min; inert gas - argon; gas flow rate - 10 mL/min; initial temperature -150°C and final temperature 200°C. Preferred polymer electrolytes were selected with T_g values either below or close to ambient temperatures.

- Using a cell equipped with gold electrodes specifically designed for this purpose ionic conductivity measurements were made for each polymer. Impedance measurements were conducted using an electrochemical impedance setup comprising PAR Potentiostat/Galvanostat Model 273 and Schlumberger SI 1260 Impedance/Gain-Phase Analyzer. Characterization included evaluation of temperature dependency of ionic conductivity to determine activation energy for lithium ion conduction within the polymer. Preliminary lithium ionic conductivities of polycarbonate siloxane polymers thus far are 8×10^{-3} S/cm at ambient temperature and 3.7×10^{-2} S/cm at 60°C.

- Selected carbonate-siloxane polymer electrolytes possessing lithium ion conductivities $> 10^{-3}$ S/cm under ambient temperature conditions were incorporated into lithium cells possessing the general configuration $Li/Li^+polymer/V_6O_{13}$ or $Li_xMn_2O_4$.

- Polymer electrolytes based upon polysiloxane with a cyclic carbonate crosslinked with methyltriacetoxysilane) demonstrated a linear response to temperature which indicates stability and reversibility whereas the response of PEO based polymers behave exponentially indicating decomposition at higher temperatures. This was a very encouraging result for our polysiloxane-cyclic carbonate polymer electrolytes thereby verifying validity for the originally proposed strategy.

- Phase II cofunding ($150,000) and Phase III follow on funding ($750,000) commitments have been obtained as a result of work performed during Phase I.

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